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AMMONIUM NITRATE: ITS PROPERTIES AND FIRE AND EXPLOSION HAZARDS

(A REVIEW WITH BIBLIOGRAPHY)

BY

G. S. SCOTT AND R. L. GRANT

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AMMONIUM NITRATE: ITS PROPERTIES AND FIRE AND EXPLOSION HAZARDS[1]

By G. S. Scott[2] and R. L. Grant[3]

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[1] The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is made: "Reprinted from Bureau of Mines Information Circular 7463."

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INTRODUCTION

Ammonium nitrate (NH_4NO_3), a white crystalline chemical compound composed of 35 percent nitrogen, 60 percent oxygen, and 5 percent hydrogen, has again attracted attention, due largely to the recent catastrophe on April 16 and 17, 1947, at Texas City, Tex. The fire and subsequent explosion on the steamship *Ocean Liberty*, outside the harbor of Brest, France, on July 28, 1947, has further increased the interest in the properties of ammonium nitrate. As a result of the Texas City disaster, several laboratories have undertaken research to determine more certainly what causes ammonium nitrate to detonate and under what circumstances. This is not the first time that ammonium nitrate has been involved in a disaster, and its properties reviewed from the standpoint of safety. The disaster at Oppau, Germany, in 1921, which involved an equimolecular mixture of ammonium nitrate and ammonium sulfate, prompted an intensive study in Europe and in America. In the United States the properties of ammonium nitrate are now of especial concern because very large quantites are being manufactured and shipped in interstate commerce and abroad. Many ammonium nitrate factories, which were built during the war, will manufacture increasing amounts of this compound for use as a fertilizer.

It is the purpose of this report to present a brief summary and bibliography of the published experimental facts about the properties and behavior of ammonium nitrate. The reader is referred to original publications for greater details of the investigative work, and for theoretical discussions. This report also includes a survey of ammonium nitrate fertilizer of the type involved in the Texas City explosions.

In the past, authorities have not always agreed on the degree of hazard involved in the manufacture and handling of ammonium nitrate, as the following quotations from the literature indicate:

Munroe (82)[4] quoted the following from Turner's Chemistry (a book published in 1835): "When this salt is exposed to fire, it liquefies, emits aqueous vapor, dries and detonates."

Berthelot (14) in his book, Explosives and Their Power, 1883, wrote: "Ammonium nitrate from the point of view of its volatility, and on account of many considerations, may be regarded as a typical explosive substance."

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[4] Numbers in parentheses refer to bibliography at the end of this paper.

Lewis and Randall (72), in their book on thermodynamics, 1923, (p. 606), stated: " . . . ammonium nitrate is not only an important component in explosives, but also in the pure state it must be regarded as dangerous. Let us consider the reaction

$$NH_4NO_3(s) = 2\ H_2O(g) + 1/2\ O_2 + N_2.$$

We have not calculated the free energy of formation of solid ammonium nitrate, but even with an aqueous solution we find for the above reaction ΔF°_{298} = -63,600, and the solid is still less stable; moreover ΔH is -28,000. It is believed that a recent explosion of unparalleled violence may have been due to careless handling of this supposedly harmless substance." [Note: When the decomposition of a substance is accompanied by a large decrease in free energy (large negative ΔF), it is potentially unstable. It may be, but is not necessarily, an explosive.]

After reviewing the results of previous investigations, Munroe (82), 1922, stated: "The foregoing record shows beyond question that ammonium nitrate under certain circumstances is, by itself, explosive." In the same paper he also stated: " . . . I believe from all the evidence thus far at hand we are justified in holding that ammonium nitrate when stored by itself in wooden receptacles and apart from explosive substances is, for transportation and storage, not an explosive."

Norman (88), 1924, stated: "I consider that ammonium nitrate is not an explosive by itself because millions of pounds of it have been and are now being made every month in Europe and in this country. . . . ammonium nitrate, in my opinion, does not constitute anything more than a fire hazard when handled by itself."

Aufschläger (6), 1924, concluded: "To summarize . . . it appears that the observed velocity of detonation of about 2,500 meters per second removes all doubt as to the character of ammonium nitrate as a brisant explosive."

Cook (29), 1924, wrote: "It is conceivable that if enough heat be applied either by direct heat, or the heat from a detonator, or the heat caused by the compression of air from a violent concussion, to pure ammonium nitrate, the liberation of oxygen and nitrogen, suddenly expanded, would cause a violent disruptive effect and that this could be propagated through a mass of the material. However, this would ordinarily require a considerable stretch of the imagination."

Parisot (91), 1939, considered pure ammonium nitrate to be a feeble explosive and its explosive character to depend upon impurities present.

Davis (34), 1945, stated: "Under favorable conditions of pressure, rapid heating, and retention of heat, ammonium nitrate may be exploded partially from heat alone near 300° C., but Munroe failed to find any instances of explosion of the salt in ordinary containers or in bulk when involved in large conflagrations of buildings or cargo vessels."

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ACCIDENTS AND DISASTERS INVOLVING AMMONIUM NITRATE

The following enumerates 18 fires, serious explosions, and disasters that have occurred since 1896, in which ammonium nitrate was involved. Of these, 5 were fires only, and 13 involved accidental explosions, most of which developed into disasters of varying magnitude. The list is given below:

1. Kensington, England, March 20, 1896

Munroe (3, 82) referred to an explosion that occurred in an enameled iron retort in which 18 pounds of ammonium nitrate were being heated to produce laughing gas for dental use. The plant was demolished. This was one of the first accidental explosions of ammonium nitrate to be reported.

2. Gibbstown, N. J., January 14, 1916 (3, 34, 82)

4,000 pounds of ammonium nitrate exploded in an evaporating pan at the Repauno works of the du Pont Co. It was thought that an air lance had become clogged, preventing agitation and thus permitting local overheating of the nitrate. This explosion killed 1 man and injured 12 others.

3. Oakdale (near Pittsburgh), Pa., September 15, 1916 (3, 34, 82)

3,000 pounds of ammonium nitrate exploded while being concentrated by evaporation in a pan at the plant of the Aetna Chemical Co. This plant manufactured ammonium nitrate from ammonia liquor and nitric acid. Although the exact cause was not ascertained, it was speculated that the nitric acid, which was recovered from TNT nitration in a nearby plant, contained small amounts of TNT or derived impurities. Although the property loss was only about $3,000, six men were killed and eight others injured, and the shock was felt 7 miles away.

4. Morgan (near South Amboy), N. J., October 4-6, 1918 (3, 34, 43, 45, 82)

Fire started in the extruding plant of the T. A. Gillespie Loading Co., where amatol shells were being loaded. Shells detonated and caused a more or less continuous bombardment for 2 days. A number of storage piles of ammonium nitrate caught fire, and some of these exploded. One ammonium nitrate explosion left a crater 150 feet long, 140 feet wide, and 30 feet deep. It was observed (82) that "all major explosions at the plant were preceded by flames which could be seen mounting higher and higher, in each case culminating in a huge column of smoke and flame, the shock of detonation reaching us a little time afterward." Some ammonium nitrate, packed in wooden barrels, had fused without exploding, and the wood had been burned away. It was stated that 9,000,000 pounds of ammonium nitrate were in the plant before the explosion. About 70 persons were killed, and the damage was estimated at about 15 million dollars.

5. Brooklyn, N. Y., April 14, 1920 (3, 34, 82)

Fire broke out on the steamer Hallfried while discharging cargo, which consisted of raw skins, paper, sodium nitrate, sodium chlorate, and 4,230,000 pounds of ammonium nitrate in casks. Although the fire was intense, and 1,944,600 pounds of the ammonium nitrate were destroyed, no explosion occurred. The fire was extinguished with water.

6. Barksdale, Wis., (about 1920) (3, 33, 34, 82)

A building containing 30,000 pounds of ammonium nitrate stored in barrels was completely burned. Some unconsumed ammonium nitrate remained after the fire. No explosion occurred.

7. Kriewald, Upper Silesia, Germany, July 26, 1921 (3, 18)

Two cars of ammonium nitrate exploded during unloading operations. Explosive charges were being used to break up the cake. Nineteen workmen were killed. The factory was demolished, leaving a crater approximately 60 feet wide and 20 feet deep.

8. Oppau (near Mannheim), Germany, September 21, 1921 (3, 24, 26, 28, 34, 45, 53, 64, 66, 107, 115)

4,500 tons of fertilizer, composed roughly of a 50:50 mixture of ammonium nitrate and ammonium sulfate, exploded during blasting with "coal-mine safety explosives" to break up the caked material. Destruction on a tremendous scale resulted. The practically new fertilizer plant was demolished, and the town of Oppau (population about 6,500) was virtually wiped out. The casualties were: 509 persons killed; 1,952 injured; 160 missing. The damage was estimated at 150,000,000 marks. A crater, 250 feet across and 50 feet deep, was produced by the explosion. It was stated that about 16,000 explosive charges had been fired in the fertilizer without mishap and that the blasting had been performed under expert supervision. Only a portion of the ammonium nitrate in the storage pile was reported to have exploded.

This catastrophe prompted an intensive investigation of the properties of ammonium nitrate in Germany and in other countries, including the United States.

9. Nixon, N. J., March 1, 1924 (3, 45, 106)

About 4,800 pounds of ammonium nitrate exploded in a vacuum grainer at the plant of the Ammonite Co., demolishing the building. The ammonium nitrate liquor had been obtained from the nearby Government arsenal at Raritan, where the ammonium nitrate had been recovered from shells and hand grenades loaded with amatol and an ammonium nitrate-nitrostarch explosive. The explosion, therefore, was believed to have resulted from the presence of TNT or nitrostarch impurities.

10. (In transit), April 4 and May 3, 1925 (3, 45, 85)

Two railroad cars in transit, containing 220 barrels each of ammonium nitrate made at Muscle Shoals, were destroyed by fire. It was assumed that the wooden barrel staves had become saturated with ammonium nitrate and that friction, caused by swaying of the cars in motion, had started the fire. There was no explosion.

11. Emporium, Pa., May 7, 1925 (3, 85)

An evaporating pan (at 270°-278° F.), containing approximately 500 pounds of ammonium nitrate, exploded at the plant of the Hercules Powder Co., destroying the building.

12. Tessenderloo, Belgium, April 29, 1942 (1, 27)

About 150 tons of ammonium nitrate exploded in the plant of the S. A. des Produits Chimiques de Tessenderloo. More than 100 persons, including all witnesses, were killed, and both the plant and the town of Tessenderloo suffered severe damage. Because it occurred in the midst of war, this disaster has only recently become known in this country. There was no evidence of fire preceding the explosion. The ammonium nitrate involved was substantially pure (34.5 percent nitrogen). Qualitative analysis of a sample of residue found in the crater after explosion gave negative tests for nitrite, hydroxylamine, hydrazine, hydrazoic acid, carbonates, sulfates, and metals, but showed traces of chlorides, phosphates, and calcium.

The actual cause of the explosion has not been established, although a thorough investigation was made by a commission of experts (1).5/ This commission believed that the only danger of an explosive reaction of ammonium nitrate existed when primed with an explosive. Since blasting charges were present in the plant for use in blasting a pile of potassium chloride, the commission inferred (in the absence of positive proof) that unauthorized blasting might have set off the explosion. It is noted, however, that the usual procedure in unloading cars of ammonium nitrate was to break up the cake with picks. There is no reason to suppose that this procedure was not being followed. It is interesting to note that the explosion at Tessenderloo, as at Oppau, was preceded by dry weather. It is also of interest to note that there was no evidence to indicate that a 10- to 15-ton pile of ammonium nitrate in the same building had detonated.

Gillet (27) has expressed the opinion that free hydrazoic acid, or some other sensitive volatile compound, may have formed in the void spaces of the ammonium nitrate and rendered the pile sensitive enough to explode under the impact of shocks from a hammer mill or picks known to be present.

5/ A limited number of copies of a translation of this article are available at the Central Experiment Station, Bureau of Mines, Pittsburgh 13, Pa.

13. Milan, Tenn. (about February 1944) (40, 43)

An explosion occurred in an evaporating pan (306°-309° F.) at the plant of the Proctor & Gamble Defense Corp. Four men were killed and 17 others injured. The cause was attributed to an oil-air mixture from the air compressor, which deflagrated in the molten ammonium nitrate which, in turn, had been contaminated with oil.

14. Texas City, Tex., April 16, 1947 (3, 45, 110)

The steamship Grandcamp exploded about 1 hour after fire was discovered in a hold containing ammonium nitrate fertilizer in paper bags. This explosion set off a chain of fires and another explosion on a nearby ship. More than 400 persons were reported killed and over 1,000 injured. The property damage amounted to many millions of dollars. Between 1,000 and 2,000 tons of ammonium nitrate fertilizer were said to have been involved in this explosion. In addition to the fertilizer, the Grandcamp contained a cargo of twine, peanuts, and oil-field machinery. According to witnesses, the fire started a little after 8:00 a.m. Initial attempts to extinguish the fire were made with containers of water, and possibly with a soda-acid extinguisher. As the fire gained headway, a water hose line was brought up, but evidently was not used because of fear of damaging the cargo. It was reported that the hold was then battened down and flooded with steam. With the fire raging out of control, the crew was ordered to abandon ship. At 9:12 a.m. the ship exploded.

15. Texas City, Tex., April 17, 1947 (3, 45, 66A, 110)

The steamship High Flyer, loaded with 960 tons of ammonium nitrate fertilizer, 2,000 tons of sulfur, and parts of knocked down boxcars, exploded at 1:10 a.m. on April 17, following a fire that broke out after the explosion on the Grandcamp. The manner in which the ammonium nitrate became ignited is unknown. It is known, however, that the adjacent hold containing sulfur was ignited and that the heat from the burning sulfur eventually caused a fire in the ammonium nitrate hold. The High Flyer exploded about 6 hours after fire was discovered in the ammonium nitrate.

Besides the two violent explosions at Texas City, there were a number of fires in which ammonium nitrate was involved. No explosions in ammonium nitrate resulted from these fires. A large quantity in Warehouse "O," for example, as well as smaller quantities in other warehouses, caught fire during the conflagration and burned without exploding. It was also reported that a freight car containing ammonium nitrate was consumed by fire without exploding.

16. Brest, France, July 28, 1947 (111)

The steamship Ocean Liberty, carrying 3,309 tons of ammonium nitrate fertilizer similar to that involved in the Texas City explosions and a variety of other materials, exploded in the harbor of Brest approximately 5 hours after the discovery of fire. The ammonium nitrate fertilizer was stowed in lower holds 1, 3, and 5. 'Tween-deck cargo in hold No. 1 included polystyrene, paraffin wax, and miscellaneous materials, some of which were combustible.

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The 'tween-deck cargo in hold No. 5 consisted of miscellaneous materials, some of which were combustible. Materials in the deck cargo over these holds included cyclohexanone, methyl ethyl ketone, rubber cement, butyl alcohol, and butyl acetate.

In fighting the fire, steam smothering was first attempted, and then water. As no progress was being made, the ship was abandoned and towed toward the sea. Twenty-one persons were reported killed and 100 injured. The city of Brest suffered heavily in property destruction.

17. Presque Isle, Maine, August 26, 1947 (2)

A fire, caused by spontaneous heating in a curing pile of mixed fertilizer, destroyed the plant of the A. W. Higgins Company. Stored in the plant were a 200-ton pile and a 40-ton pile of ammonium nitrate, "Aeroprills." Some of the ammonium nitrate was dissolved and lost by the water used in fighting the fire. Some of it was consumed by the fire, burning with difficulty and without incident in that there were no explosions. The balance of the ammonium nitrate remained in good condition and was recovered. Damage to the property was estimated at $100,000.

18. St. Stephen, Canada, 1947 (12)

A fire occurred in the plant of the Summers Fertilizer Company under circumstances apparently similar to those in the Higgins fire (above). In the Summers fire, however, there were 400 tons of ammonium nitrate stored in the plant, all of which was consumed by the fire without exploding.

At least 11 fires involving carlot quantities of ammonium nitrate in transit are known to have occurred, none of which exploded (59).

MANUFACTURE OF AMMONIUM NITRATE (57, 76)

Ammonium nitrate is made by neutralizing ammonia with nitric acid. The ammonia is obtained as a byproduct in coke manufacture or made synthetically from its elements, the nitrogen derived from air liquefaction and the hydrogen from water gas, coke-oven gas, natural gas, fermentation, or the electrolysis of water (93). The nitric acid is made by distilling a mixture of sulfuric acid and a nitrate, such as sodium or potassium nitrate, or by catalytic oxidation of ammonia in air.

The production of ammonium nitrate has increased sharply in recent years. It was reported (59) that during the 1946-47 season 845,000 tons were produced in United States plants.

The conversion of ammonium nitrate plants used to produce wartime explosives to peacetime production of fertilizers has stimulated the investigation of methods for utilizing ammonium nitrate for this purpose. Numerous formulas have been suggested (96) and patents issued for overcoming the caking properties of this compound.

PREPARATION OF AMMONIUM NITRATE FERTILIZER

The process given below refers particularly to the type of fertilizer involved in the Texas City and Brest disasters (56).

Starting with ammonium nitrate liquor of about 80 percent strength, the crystals are dissolved by steam. The warm liquor is then filtered and transferred to the hi-pans, which are open steam-heated evaporating pans with air agitation. When the "fudge" point (310° F.) is reached, the nitrate is transferred to the graining kettles, where it is cooled while being mechanically agitated. When the granulation reaches a certain point, coating material is added and stirring continued until the coating is uniform. [It is interesting to note that a patent was issued as far back as 1885 for coating ammonium nitrate with petrolatum (82).] The material larger than 8-mesh is then screened out, and the material under 8-mesh is bagged in 6-ply moistureproof paper bags at a temperature not exceeding 200° F.

The finished fertilizer is required to meet the following specifications:

Moisture	0.25% maximum
Ether-soluble material (wax)[1]	0.75% ± 0.35%
Water-insoluble material (clay)[2]	3.50% ± 1.00%
Total nitrogen	32.50% minimum

[1] A saturated white paraffin wax.

[2] Kieselguhr.

Specifications for granulation are:

Through U. S. Standard No. 8 sieve	100% minimum
On U. S. Standard No. 35 sieve	55% minimum
Through U. S. Standard No. 100 sieve	8% maximum

It should be mentioned that, after the First World War, ammonium nitrate was recovered from the explosive, "Amatol," a mixture of ammonium nitrate and TNT (106), by dissolving the ammonium nitrate with steam, then separating it from the liquid TNT. After further purification of the ammonium nitrate it was used in the manufacture of fertilizer. This process is now believed to be hazardous.

PHYSICAL PROPERTIES OF PURE AMMONIUM NITRATE

Ammonium nitrate (NH_4NO_3), 35 percent nitrogen, molecular weight 80, oxygen balance plus 20 percent,[6] is ordinarily a white crystalline solid of the orthorhombic system. It has a melting point of 169.6° C. (337° F.). It is reported to have a slow decomposition point at about 200° C. (392° F.) (26) and a boiling point of 180° C. (356° F.) under the vacuum of the Sprengel pump, while at some point between 260° and 300° C. (500°-572° F.) the decomposition may become explosive. Its usual packing density is between 0.8 and

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[6] The oxygen balance refers to the amount of oxygen in an explosive, greater than, or less than that required for complete combustion of the combustible materials present. In the case of ammonium nitrate it is based on the reaction:

$$NH_4NO_3 = N_2 + 2\ H_2O + 1/2\ O_2.$$

Here 1/2 O_2 (20 percent of the weight of the ammonium nitrate), is available for the combustion of other material.

0.9 gram per cubic centimeter, depending upon particle size and pressure applied, while the density of the crystals is 1.72. The crystals have a hardness of about 1.1 on Mohs' scale.

Crystalline Forms

Ammonium nitrate may exist in several crystalline forms, depending upon temperature and pressure. Figure 1 is a plot of Bridgman's data (19), showing six different crystalline forms in the solid state. Mellor (77) states that neither Lehman nor Behn could detect any signs of further transformation between -18° C. and -140° C. Crenshaw and Ritter (30), however, showed a transformation at -60.4° C., on the basis of specific-heat measurements.

Bowen (17) gives the transition temperatures and crystalline forms at atmospheric pressure as follows (54, 97):

Melting point	169.6° C.
I. Cubic	125.2° to 169.6° C.
II. Tetragonal	84.2° to 125.2° C.
III. Orthorhombic (?)	32.1° to 84.2° C.
IV. Orthorhombic	-16° to 32.1° C.
V. Tetragonal	Below -16° C.

Bridgman gives a series of tables showing volume changes, latent heats, and energy changes for the different transformations shown on figure 1. The maximum energy of transformation given is 5.53 kilogram-meters per gram (= 13.0 calories per gram).

Hendricks (54) found form III to be orthorhombic, and form V to exist down to -18° C. instead of -16°, and stated: "Diffraction patterns of samples at -33° and -78° are identical save for displacement due to expansion, despite the existence of a gradual transition at ca, -60°."

Hygroscopicity (37, 78, 96, 97)

Ammonium nitrate may either take up from or give off water to the atmosphere, depending upon temperature and relative humidity. This property causes caking of the salt. Figure 2 shows a plot of data taken from (97).

Solubility

The solubility of ammonium nitrate in water is given in the following table. The data have been converted from Seidell's (97, 101) grams per 100 grams of water and from the mole fraction given in the Internation Critical Tables (60) to percentages by weight of the salt in water solutions.

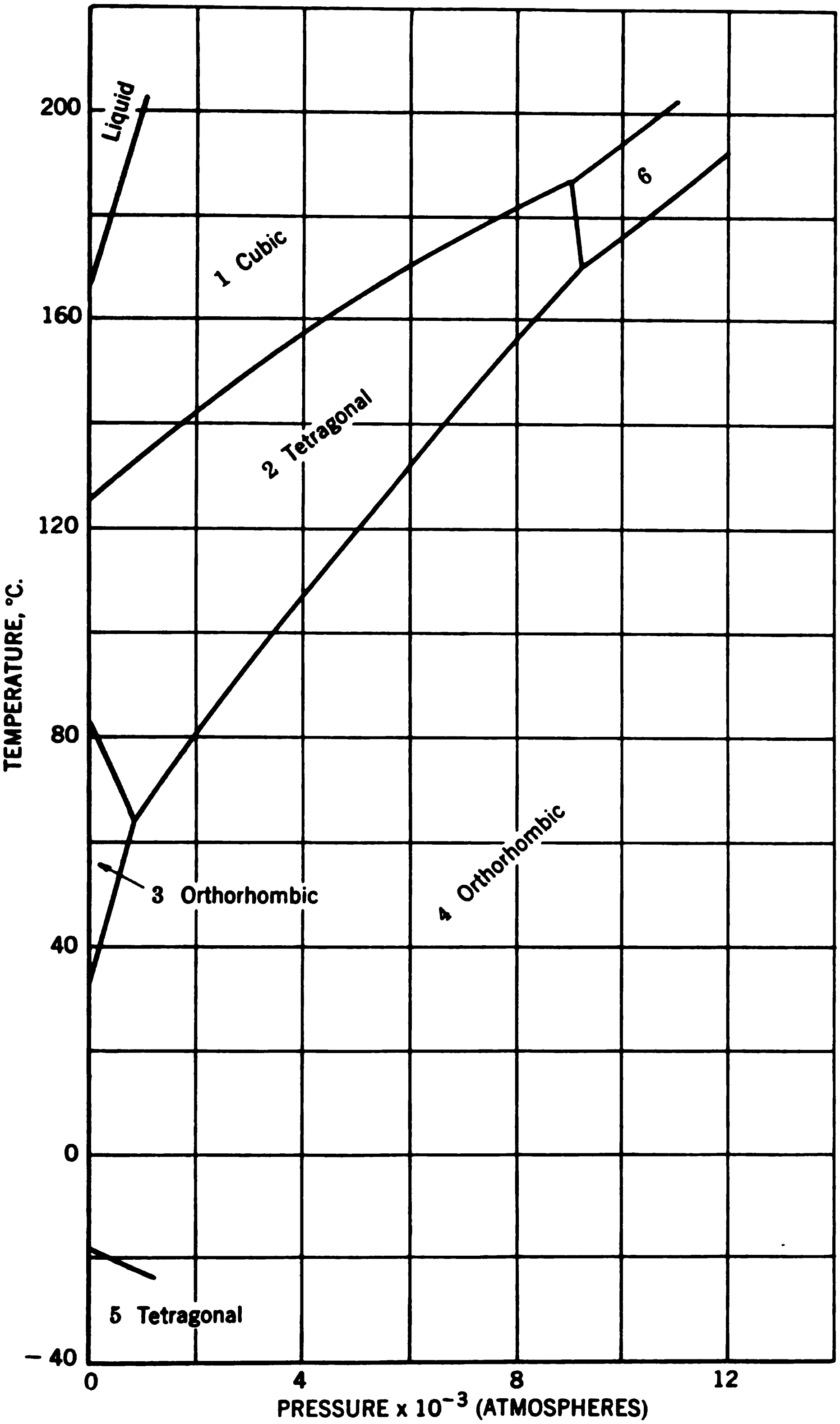

Figure I. - Allotropic forms of ammonium nitrate. (From Bridgman.)

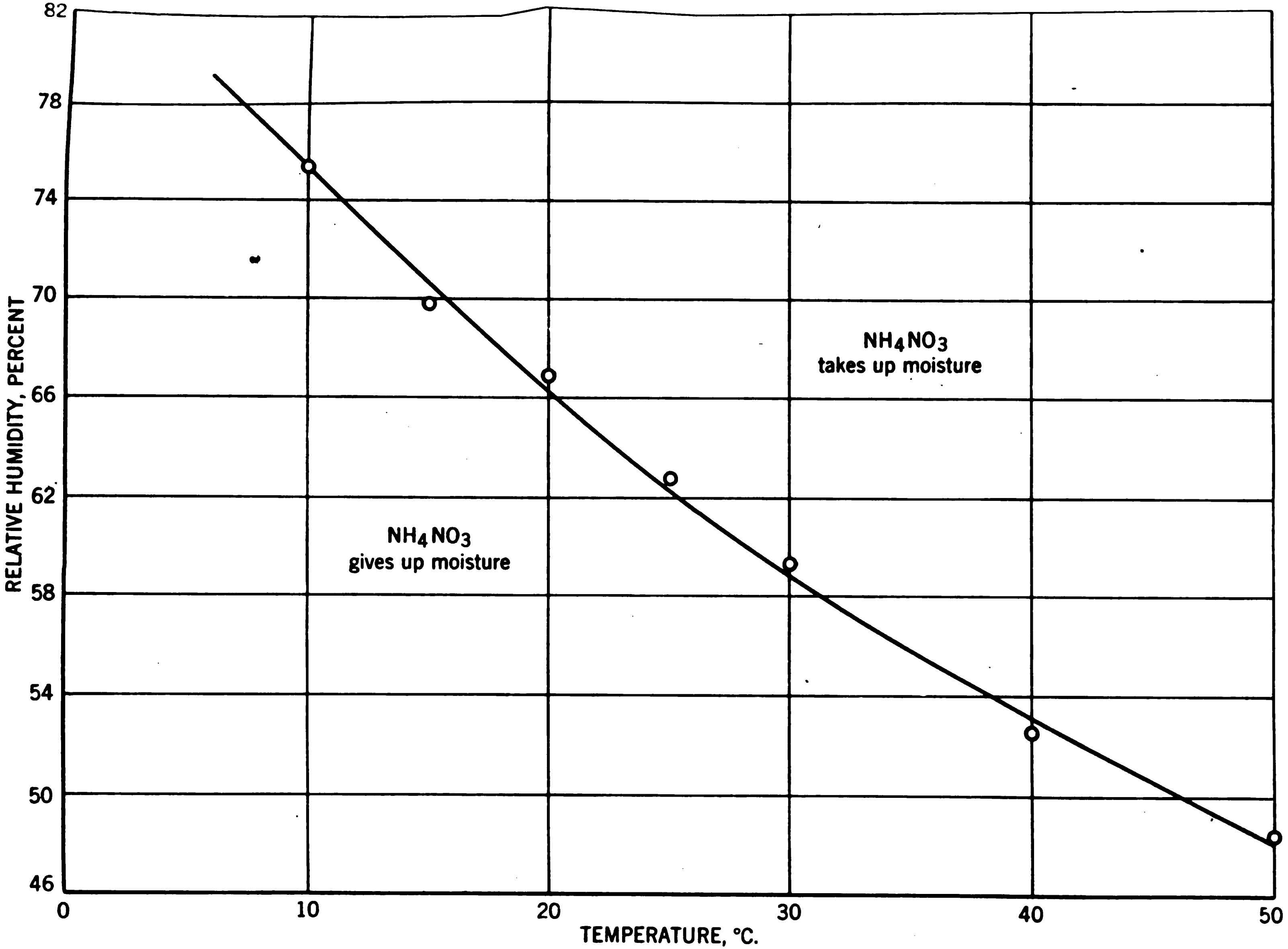

Figure 2. - Relative humidity in the air in equilibrium with saturated ammonium nitrate. (From Ross, etc.)

Solubility of Ammonium Nitrate in Water

Temperature, °C.	Solubility, percent by weight	
	Seidell	Int. Crit. Tables
-20		40.0
-10		48.4
0	54.1	55.4
10		61.2
20	65.7	66.1
30		70.4
40	74.8	74.1
60	80.8	80.6
80	85.3	86.5
90		89.0
100	89.7	91.2
140		97.4
160		99.2
169		100.0

Specific Gravity (77)

The specific gravity of the solid is given as 1.684 - 1.791 (15°-23° C.). The specific gravity of the liquid is reported as 1.36 at 200° C. The specific gravity of aqueous solutions at 0° and at 100° C. are reported as follows:

Ammonium nitrate, percent by weight	Specific gravity	
	At 0° C.	At 100° C.
2.00	1.011	0.9680
5.00	1.022	.9780
10.00	1.046	.9988
19.77	1.091	1.0372
30.33	1.139	1.0830
40.15	1.186	1.1258
50.16	1.238	1.1755
59.94	1.293	1.2288

Specific Heat

Values taken from the work of Behn (10) are as follows; (see also fig. 4):

Temperature, °C.	Crystalline Form	Specific heat, calorie per gram per °C.
-15 to 15	Orthorhombic	0.395
-79 to -20	Tetragonal	.352
-190 to 25	Tetragonal and orthorhombic	.305
-190 to -20	Tetragonal	.274

For crystalline form V (tetragonal), he states that the equation:

$$C_p = 0.423 + 0.00143\ t$$

holds between -190° and 20° C., where t is the centigrade temperature. For form IV (orthorhombic) he gives the mean specific heat as 0.407 calorie per gram between 0° and 31° C.

Crenshaw and Ritter (30) give specific-heat data for ammonium nitrate between -90° and 0° C. Their data (shown on fig. 4) are somewhat higher than Behn's. For example, at 0° C. their value is 40.64 calories per mole (0.508 calorie per gram). They recorded a transformation at -60.4° C., with a transformation energy of 530 calories per gram.

Thermal Conductivity

A reference in Chemical Abstracts, vol. 32, 1938, page 417, to a Russian article by Golubev and Lavrent'eva (50) quotes a value of the thermal conductivity of ammonium nitrate of 0.205 kg.-cal./meter/hr./°C. This is equivalent to 0.1375 B.t.u./ft./hr./°F.

Electrical Conductivity

The electrical conductivity of the molten salt is given (77) as 0.320 reciprocal ohm at 172° C., 0.397 at 202°, and 0.447 at 213°. At any temperature, t (°C.), between 160° and 220° C., the electrical conductivity is given by the expression: $0.400 \, [1 + 0.0073 \, (t - 200)]$.

Crushing Strength

Ross and associates (96) state that 1 percent of moisture so weakens ammonium nitrate crystals that they become compressed together in a solid mass under a pressure of 12 pounds per square inch. They found that, after being subjected to changing humidities, ammonium nitrate cake could have a crushing strength as high as 500 pounds per square inch.

DECOMPOSITION OF AMMONIUM NITRATE BY HEAT

Berthelot (14), 1883, studied the decomposition of ammonium nitrate by heat, and his work has been frequently quoted (33, 34, 82). He lists the following reactions for decomposition of ammonium nitrate:

(1) $NH_4NO_3 = HNO_3 + NH_3$ (absorbs 41,730 calories)
(2) $NH_4NO_3 = N_2 + 1/2 \, O_2 + 2 \, H_2O$ (liberates 28,470 calories).
(3) $NH_4NO_3 = N_2O + 2 \, H_2O$ (liberates 8,820 calories).
(4) $NH_4NO_3 = 1/2 \, N_2 + NO + 2 \, H_2O$ (liberates 6,870 calories).
(5) $3 \, NH_4NO_3 = 2 \, N_2 + N_2O_3 + 6 \, H_2O$ (liberates 65,420 calories).
(6) $2 \, NH_4NO_3 = 1\text{-}1/2 \, N_2 + NO_2 + 4 \, H_2O$ (liberates 48,910 calories).
(7) $5 \, NH_4NO_3 = 2 \, HNO_3 + 4 \, N_2 + 9 \, H_2O$ (liberates 153,360 calories).

In the above equations, the nitrate is solid, and all products are gaseous. The heat liberated is at constant pressure and at 18° C. The reaction energies were calculated by the authors from the data of Bichowsky and Rossini (15).

All of these reactions do not take place either simultaneously or consecutively. Some idea of the manner in which they occur may be had from the following quotations from Berthelot and from the work of other investigators. Concerning reaction 1, for example, Berthlot stated on page 5: "The dissociation of fused or even gaseous ammonium nitrate into gaseous nitric acid and ammonia . . . seems to be first produced and at a low temperature." Again, on page 6: " . . . If the salt be supposed to be previously decomposed into gaseous nitric acid and ammonia . . ." On page 410: "This salt commences to decompose a little above 100°, not without being partly sublimed."

Findlay and Rosebourne (44), however, heated the salt 100 days at 100° C. and found no appreciable decomposition.

Tramm and Velde (109) found that, when free of chlorides, ammonium nitrate may be held at 175° for a long time without decomposition but that relatively small quantities of chlorides and free acid may cause decomposition at temperatures as low as 140° C.

Saunders (99) stated: "Pure dry ammonium nitrate decomposes only slowly at 200° . . . . The nitrate first melts at 169°, then dissociates into nitric acid and ammonia, and begins to evolve a gas containing 98 percent of nitrous oxide." (The other 2 percent was practically all N_2.)

Berthelot and Saunders agree with respect to reaction 3, for Berthelot stated on page 410: "Toward 200°, it separates in a sufficiently definite manner into nitrogen monoxide and water without, however, there being a fixed temperature at which this destruction takes place."

Shah and Oza (102), Kaiser (62), and Saunders all reported free nitric acid in the residue (210°-300° C.).

Tramm and Velde, and Davis (see under "Spontaneous Heating") agree that ammonia retards the decomposition, and Friedrich (47) patented this principle for the production of nitrous oxide from ammonium nitrate.

Concerning the remaining reactions, Berthelot stated on page 6: "When rapidly heated, the explosive decompositions, properly so-called, of ammonium nitrate take place; one of them produces nitrogen and oxygen

$$NH_4NO_3 = N_2 + O + 2\ H_2O.$$

Nitrogen and nitrogen dioxide are also formed:

$$2\ NH_4NO_3 = N_2O_2 + N_2 + 4\ H_2O.$$

Heat is also liberated when ammonium nitrate gives rise to nitrogen, water, and nitrogen tetroxide

$$4\ NH_4NO_3 = 3\ N_2 + N_2O_4 + 8\ H_2O.$$

"The ammonium nitrate may also be conceived as being transformed into nitrogen, water, and nitrogen trioxide

$$3\ NH_4NO_3 = 2\ N_2 + N_2O_3 + 6\ H_2O,$$

etc." On page 410: "A sudden decomposition yields at the same time as nitrogen monoxide, various products corresponding to simultaneous decompositions, so that ammonium nitrate can undergo eight distinct transformations, several of which are simultaneous in certain explosive decompositions."

On page 244: " . . . the reaction becomes explosive at the time that the multiple products appear that are due to the many distinct modes of simultaneous decomposition, such as are shown on page 5 . . ."

Saunders gives the following equations as describing the course of the decomposition (between 210° and 260° C.):

$$(1)\quad NH_4NO_3 = NH_3 + HNO_3$$
$$(2)\quad NH_4NO_3 = N_2O + 2\ H_2O$$
$$(3)\quad 5\ NH_3 + 3\ HNO_3 = 9\ H_2O + 4\ N_2.$$

He considers the second to be the main change, and bases the third upon always finding the residual liquid to be acid. (This would account for the 2 percent nitrogen noted above.)

In 1830, Emmett (41) stated that, when exposed to air or when heated, ammonium nitrate loses ammonia and becomes acid.

In analyzing residual gases after gas-phase explosions, Saunders found nitrogen dioxide, nitric oxide, and nitrogen in the ratio 2 : 4 : 5 and postulated an over-all reaction:

$$8\ NH_4NO_3 = 16\ H_2O + 2\ NO_2 + 4\ NO + 5\ N_2.$$

If half of the nitrate is decomposed according to Berthelot's equation 4 and the other half according to his equation 6, the result would be the same as that given by Saunders. Saunders stated that no oxygen was found in any case, when discussing his results up to 260° C., and apparently this also includes the explosive decomposition. This would seem to raise some question concerning Berthelot's equation 2.

Concerning the temperature at which the decomposition becomes explosive, Saunders stated: "At some point near 300° other oxides of nitrogen are evolved, the action proceeding explosively." Berthelot stated that, if superheated above 230° C., the decomposition accelerates itself and ends by becoming explosive. (Note also, the "explosion temperature" under "Effect of Heat, Confinement, and Quantity.")

Davis (34) stated that not until the decomposing mass reaches about 260°-350° C. does the reaction become sufficiently exothermic to produce heat in excess of that absorbed by adjacent quantities of decomposing salt.

Kaiser (62) found very slow decomposition at 200° C., rapid decomposition at 260°. He stated that, after the appearance of fog and a considerable delay between 260° and 269°, an explosion occurred. He gave the reaction:

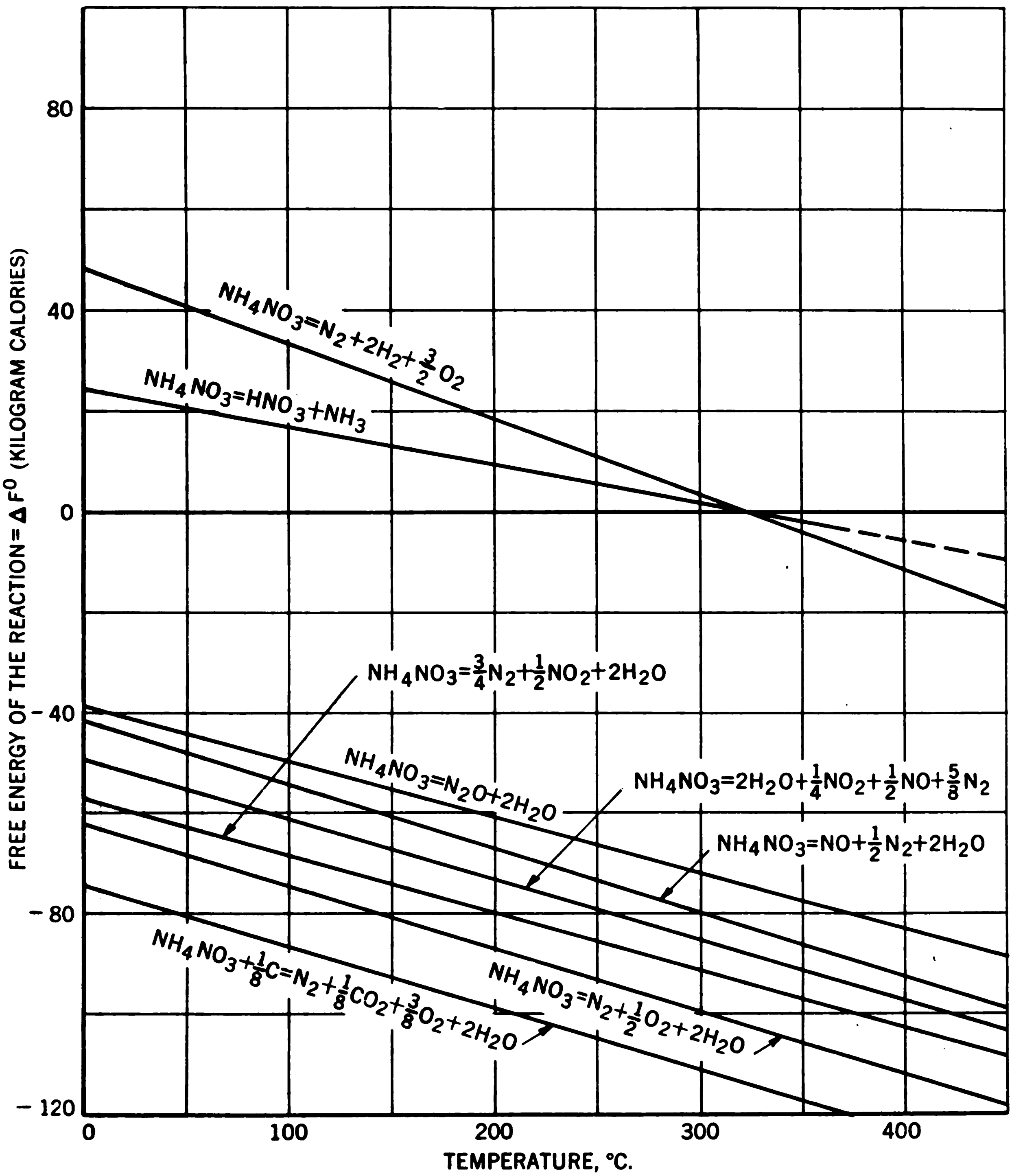

Figure 3. - Free energies of some decomposition reactions of ammonium nitrate. (Positive values indicate stability.)

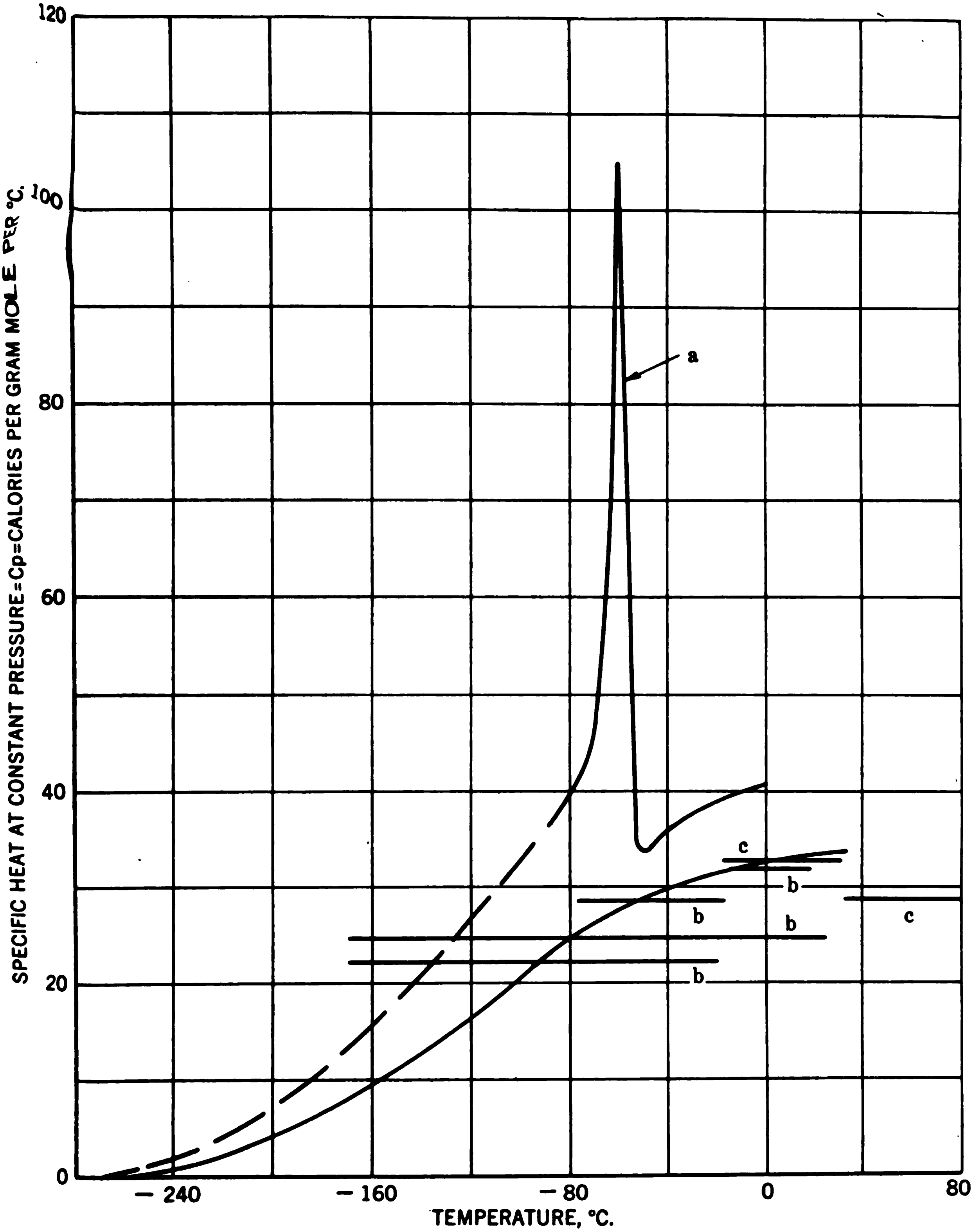

Figure 4. - Specific heat of ammonium nitrate. (a) Crenshaw and Ritter (1932), (b) Behn (1908), (c) Bellati (1886).

$$4\ NH_4NO_3 = 2\ NH_3 + 3\ NO_2 + NO + N_2 + 5\ H_2O.$$

Kast (65) stated that, when pure ammonium nitrate was heated to 180°, it melted; when heated further to 220°, it gave off bright-gray vapors; and between 245° and 340° frothing and decomposition ensued, with development of reddish brown vapors.

Energy Relations

Lewis and Randall (72) stated (p. 606): "It is true we do not recognize as explosives all substances whose decomposition would be attended by large negative values of ΔF (free energy) and ΔH (heat of reaction). Nevertheless they belong at least potentially to this class." Accordingly, calculations of free energies will indicate whether or not ammonium nitrate may be classified as a potential explosive. The system of Lewis and Randall was used in the following calculations.

Figure 3 shows a plot of free energies versus temperature for a number of decomposition reactions involving ammonium nitrate. It will be noted that this salt is stable up to about 320° with respect to its elements and also with respect to its dissociation into ammonia and nitric acid. It is not stable, however, with respect to the various decompositions accomplished by the formation of water. If, therefore, the decomposition of ammonium nitrate follows any of these latter reactions, it could conceivably become explosive. As the various oxides of nitrogen are unstable, it follows that the largest free-energy decrease occurs for decomposition into water, nitrogen, and oxygen. When carbonaceous matter is present and reacts with the liberated oxygen, a still greater free energy decrease takes place.

The data for the curves were computed by the authors from existing thermal data, with one exception - the ammonium nitrate itself. The heat of formation of solid ammonium nitrate is given as -88,060 calories per gram mole at 25° C. (72). No free-energy or entropy data could be found. The specific heats previously mentioned were plotted as shown in figure 4 and extrapolated to zero absolute. The entropy at 298° K. was then obtained by replotting specific heats against natural logarithms of absolute temperatures, and integrating with a planimeter.

The values obtained were 27.1 e.u. when using Behn's data (10) and 41.8 e.u. when using Crenshaw and Ritter's data (30). Free energies calculated from these figures and the heat of formation at 298° K. were -47,920 and -43,539 calories per mole, respectively. Lewis and Randall calculated the free energy of the equation

$$NH_4NO_3(s) = 2\ H_2O(g) + 1/2\ O_2 + N_2$$

to be -63,600 when in solution, and stated that the solid is still less stable. Using the above free energies of formation of ammonium nitrate, the authors obtained

$$\Delta F^o_{298} = -61,094 \text{ and } -65,475,$$

respectively, for this equation. It was then assumed that -65,475 was the better value since it conformed with value and statement of Lewis and Randall.

Specific-heat data up to 100° C. were used to obtain a specific-heat equation and then a free-energy equation, which was used to calculate free energies up to 400° C.

EFFECT OF IMPURITIES ON DECOMPOSITION OF AMMONIUM NITRATE

According to Mellor (77), fused ammonium nitrate will react with aluminum, zinc, lead, antimony, bismuth, nickel, copper, silver, and cadmium but will not react with arsenic, tin, iron, or mercury. Zinc is attacked very rapidly. Copper is said to produce nitrite and thereby increase the explosibility (34). Aluminum, iron, and zinc powders lower the decomposition temperature of ammonium nitrate, as does organic matter (33, 65).

It is stated that seven different chromium compounds, in quantities from 1 to 20 percent, catalyze the decomposition of ammonium nitrate (75).

Decomposition is reported to be promoted by the presence of cellulose or starch (44).

Kast (65) refers to a fire in Witten in 1906, involving ammonium nitrate plus a small amount of added potassium permanganate. Spontaneous heating was given as the cause of the fire.

OXIDIZING PROPERTIES

Ammonium nitrate, like sodium nitrate, potassium nitrate, and other nitrates, is an energetic oxidizing agent (16, 33, 41, 44, 77, 82) containing 20 percent of its weight as available oxygen when decomposed according to the equation

$$NH_4NO_3 = N_2 + 2\ H_2O + 1/2\ O_2.$$

Organic or other easily oxidizable matter in contact with ammonium nitrate produces violent combustion on ignition (34).

Various metals react with ammonium nitrate at elevated temperatures (40) and some at ordinary temperatures (16, 34) - especially zinc (16).

Hardesty and Davis (52) have shown that, in the presence of any material that can cause ammonium nitrate to set free nitric acid, the following reactions with carbonaceous material are possible:

$$2\ HNO_3 + C = CO_2 + H_2O + NO_2 + NO$$

$$2\ NO_2 + 2\ NO + 3\ C = 3\ CO_2 + 2\ N_2.$$

The above reactions can take place in the presence of peanut-hull meal, cottonseed meal, soybean meal, lignin, cocoa-shell meal, lignite, dried peat, sawdust, ground cork, ground kraft paper, ground burlap, castor pomace, millet seed, oak-heart wood, brown rotted wood, cane sugar, dextrose, and cornstarch.

They found the gaseous products from the oxidation of peanut-hull meal by ammonium nitrate at 30° C. to consist of:

	Percent
Nitrogen (N_2)	43.5
Oxygen (O_2)	1.7
Carbon Dioxide (CO_2)	42.3
Argon (A)	.1
Nitrous Oxide (N_2O)	12.2
Nitrogen Dioxide (NO_2)	.1
Cyanogen (C_2N_2)	.1
	100.0

It is important to note that, in the oxidation of organic matter, metal powders, etc., by ammonium nitrate, the presence of air is not necessary as the oxygen can be furnished by the ammonium nitrate. Thus an ammonium nitrate fire cannot be extinguished by smothering, such as flooding with steam.

SPONTANEOUS HEATING

As far as is known, there is no recorded instance of spontaneous heating in pure ammonium nitrate. In fact, as mentioned, Findlay and Rosebourne (44) found no decomposition of the salt when heated at 100° C. for 100 days.

However, in the presence of foreign material, spontaneous heating may take place, depending upon the conditions, such as quantity, temperature, insulating properties, nature of the foreign material, etc.

A study in which a large quantity of ammonium nitrate fertilizer was exposed to temperatures ranging from 72° to 100° F. was made by one of the authors (G.S.S.). This was carried out on shipboard during loading and in transit across the Gulf of Mexico and the Caribbean Sea to the Canal Zone. Data collected (100) showed no indication of self-heating in the 8,500-ton cargo during the 9 days of loading or during the 5 days in transit. Information was received later from an Asiatic port stating that the cargo had reached its destination at essentially the same temperature as recorded at the termination of the tests.

Davis and Hardesty (36) found that free acid promoted combustion and that ammonia retarded it, when ammonium nitrate and combustible material are in contact. They report (52) that 3 kilograms of a mixture of 7 parts superphosphate, 2 parts ammonium nitrate, and 1 part peanut-hull meal in the presence of 6.16 percent free acid, stored in a Dewar flask at 30° C., ignited after 13 days and 19 hours. Increase in acid concentration increases the oxidation rate. For example, 50 grams of ammonium nitrate and 100 grams of peanut-hull meal in the presence of 25 grams of water containing 60 percent free acid ignited in 2 hours after storing in a Dewar flask at 30° C.; 147 grams of a mixture of 200 parts peanut-hull meal, 100 parts phosphoric acid, 400 parts ammonium nitrate, and 35 parts water, stored in a 200-cc. Dewar flask at 30° C., reached a temperature of 425° C. in 15 hours.

Easily oxidizable metal powders in contact with wet ammonium nitrate may heat spontaneously (16, 34).

When initially at 150° C., ammonium nitrate fertilizer plus 10 percent sawdust can ignite in 50 minutes (75).

The paraffin-type coating materials used in the manufacture of ammonium nitrate fertilizer apparently make little or no contribution to spontaneous heating. T. H. Wilde, quoted by Davis (34), observed no change in temperature in 2 weeks in ammonium nitrate containing 0.5 percent petrolatum-rosin-paraffin wax stored in a thermos bottle at 60° C.

According to plant experience (56), fertilizer packed in the multiwalled paper bags at 93° C. (199° F.) does not heat further. If packed at 104° C. (219° F.) and loaded promptly into railroad cars, the asphalt in the bags begins to "bleed." If packed at 110° C. (230° F.), the insides of the bags show charring, particularly if heat losses are minimized. At 118° C. (244° F.) the three inner sheets are considerably weakened by charring and embrittlement. At 150° C. (302° F.) simulated bags ignited spontaneously in 5 or 6 hours.

Experimental work (75) has shown that at 100° C. (212° F.) there was little or no reaction in ammonium nitrate fertilizer - bag paper mixture occurs in 16 days. At 100° C. (212° F.) there was little or no reaction, but at 120° C. (248° F.) the ammonium nitrate was found to react markedly with bag paper, sawdust, iron powder, or sawdust and oil.

DETONATION OF AMMONIUM NITRATE

Detonation Rates

Ammonium nitrate has been reported to have rates of detonation ranging from as low as 1,000 to as high as 2,700 meters per second, depending upon the conditions. (See table 1.) The more important of these contributing factors are confinement, pressure, charge diameter, strength of initiating impulse (that is, the nature and quantity of booster), packing density, particle size (especially at low packing densities), temperature, and the presence of small amounts of certain contaminants.

The detonation rate decreases with decrease in tube diameter (71).

Kast (65) postulated that ammonium nitrate did not ordinarily develop its full inherent explosive power and that the limiting value of the detonation rate was seldom reached in the testing methods used. He gave the following calculated values to represent incomplete and complete detonation of ammonium nitrate:

	For incomplete detonation	For complete detonation
Detonation rate, meters per second	1,500	3,000
Gas volume for 1 kilogram, liters	945	980

Sensitivity to Friction and Impact

In 190 tests, Munroe (34, 82) was unable to obtain an explosion of ammonium nitrate by friction.

TABLE 1. - Detonation rates of ammonium nitrate and ammonium nitrate fertilizer

Rate	Density	Diameter of charge	Container	Method of initiation	Remarks	Reference
m./s.	g./cc.					
				Ammonium nitrate		
1,270	-	40 mm.	Steel tube, wall thickness not given	5 No. 8 detonators	-	Aufschläger (6)
2,440	-	50 mm.	Lead tube, wall thickness not given	Compressed picric acid	-	Do.
1,000	0.71	1-1/32 in.	Shelby steel tube. 1-1/32 in. I.D., 1-1/2 in. O.D.	No. 8 det. with various boosters (picric acid, tetryl, TNT, amatol)	15° C.	Gawthrop (48)
1,700	.71	1-1/32 in.	do.	do.	140° C.	Do.
1,400 to 1,500	1.0	7.2 to 8 mm.	Tubes	Nitrate mixed with 1.5-2.0% of Mg.Al. di- and trinitronaphthalenes, TNT. Rate of pure ammonium nitrate found by extrapolation.		Laffitte (71)
1,850	.82	1-1/32	Shelby steel tube, wall thickness 3/16 in.	No. 8 det. plus 100 g. tetryl	Pure nitrate	Perrott (92)
1,940	.82	1-1/32	do.	do.	1% nitrostarch	Do.
2,060	.82	1-1/32	do.	do.	5% nitrostarch	Do.
2,470	.82	1-1/32	do.	do.	10% nitrostarch	Do.
1,460	.83	2.5 cm.	Seamless steel tube	50 gm. pressed tetryl	-	Kast (65)
1,310	.84	2.5 cm.	do.	do.	-	Do.
1,470	.83	2.6 cm.	do.	60 gm. pressed tetryl	-	Do.
1,230	.69	5 cm.	do.	100 gm.pressed picric acid	-	Do.
1,280	.65	5 cm.	do.	do.	-	Do.
1,490	.68	8 cm.	do.	300 gm.pressed picric acid	-	Do.
1,500	.66	8 cm.	do.	do.	-	Do.
1,530	.79	8 cm.	do.	100 gm.pressed picric acid	-	Do.
1,550	.88	8 cm.	do.	do.	-	Do.
2,700	.98	8 cm.	do.	250 gm.pressed tetryl	-	Do.
1,920	.64	10 cm.	do.	100 gm.pressed picric acid	-	Do.
1,820	.84	10 cm.	do.	200 gm.pressed tetryl	-	Do.
				Ammonium nitrate fertilizer		
1,106	.90	4-1/2 in.	Unconfined	1/2 lb. Comp. C.	Length of column, 48 in.	Macy (75)
1,350	.91	1-1/4 in.	Seamless steel tubing 1/4 in. wall thickness	Blasting cap and 50 g. Comp.A-3 (U.S.Eng.Special)	Length of column, 51 in.	Do.
2,109	1.4	3 cm.	Molten (above 169° C.)	do.	Length of column, 44 cm.	Do.

Munroe, dropping a 20-kg. weight 1 meter onto ammonium nitrate, obtained no explosion in 10 tests. Jones (61) dropped a 200-kg. weight 7.5 meters on ammonium nitrate at 140° C. without explosion. Macy and associates (75) obtained no explosion when a 52-pound weight was dropped 10 feet onto a mixture of molten ammonium nitrate fertilizer with 5-percent bag paper contained in a steel pipe.

However, explosions were obtained by these investigators (at least 1 explosion in 10 trials) when a 2-kg. weight was dropped from a height of 31 inches onto a piston which transmitted the impact to 0.001-gram samples of ammonium nitrate or ammonium nitrate fertilizer contained in concave steel cups at 25° C. At 175° C., explosions were obtained when the weight was dropped from a height of 12 inches.

A 200-kg. weight was dropped 25 feet onto ammonium nitrate (approximately 17 grams) at the Bureau of Mines Explosives Testing Station without causing an explosion (22).

Kast (65), however, reported an explosion of ammonium nitrate by impact with the 10-kg. weight at 20 cm.

Sherrick (105), in compressing ammonium nitrate for his tests, subjected it to pressures up to 7,000 p.s.i. at 20° C. for 30-second periods. No accident was reported.

Sensitivity to Detonators and Boosters

Bashford (7) stated that ammonium nitrate was very difficult to detonate but that it could be detonated by fulminate caps. Munroe noted a damping effect in an open trough having a square cross section of 5-1/2 inches. One of the authors (R.L.G.) demonstrated this relative insensitivity to detonation by firing 5-gram charges of chemically pure ammonium nitrate, density 0.84, with No. 6 to No. 10 fulminate-chlorate (80-20) detonators, using small paper cartridges in the sand bomb, similar to the miniature cartridge tests (51). Similar tests were made with pure TNT, density 0.94. The results are given in table 2 below (22):

TABLE 2. - Detonation of ammonium nitrate and TNT

Cap	Weight of fulminate-chlorate in detonator, grams	Sand crushed by 5 grams of: Ammonium nitrate, grams	Sand crushed by 5 grams of: TNT grams
No. 6	1.0	21	253
No. 8	2.0	43	254
No. 10	3.0	58	261

It is apparent that only a small fraction of the 5 grams of ammonium nitrate was brought to detonation, whereas the TNT detonated substantially completely under similar conditions. These results were corrected for the detonator effect.

In the well-known ballistic mortar test, however, results were obtained indicating that pure ammonium nitrate will detonate completely with a No. 6 fulminate detonator (22). These data also illustrate the importance of confinement.

Sherrick (104, 105) and Gawthrop (48) have shown that the detonation of small quantities of ammonium nitrate (8.6 cubic inches) at ordinary temperatures depends upon the effectiveness of the booster. Jones has shown that the sensitivity of 100-gram charges to detonation by means of detonators and booster charges increases with increase in temperature (61). The lead-block compression increased threefold between 10° and 140° C. Munroe also noted that increase in temperature increases the sensitivity to detonation.

Aufschläger (6) detonated 3.5 kg. and 12.0 kg. of ammonium nitrate in cardboard boxes. He stated that the initial impulse must be strong enough. Bramkamp (18) detonated 200 grams of ammonium nitrate with a No. 8 detonator and a mixture of 47 grams of ammonium nitrate and 2 grams of TNT. Munroe (82) detonated 135 pounds of ammonium nitrate with 243 grams of blasting gelatin. The crater produced by this detonation was 12 feet in diameter and 4 feet in depth.

It is interesting to note at this point that, in many of the ammonium nitrate explosions, not all of the nitrate exploded, and frequently adjacent piles failed to detonate. For example, in the explosion at Nixon, N. J., approximately 4,800 pounds of ammonium nitrate exploded but failed to detonate some 300 tons of coated nitrate in the other end of the building - perhaps 100 feet from the center of the explosion (106). Similar observations were made at Morgan, N. J., and at Texas City, as well as at Oppau.

Effect of Heat, Confinement, and Quantity on Explosibility of Ammonium Nitrate

Belayev and Chariton (11) stated that stable detonation can be obtained in ammonium nitrate (density, 0.7-0.8) provided that the charge diameter is 80-100 mm. or more and that it can be detonated in smaller diameters, provided the casing is sufficiently strong. They obtained the diameter value of 80-100 mm. with thin-walled glass, or cardboard casing. Their initiator was 3 percent TNT and 97 percent ammonium nitrate.

Sherrick (104) stated that confinement is very effective in promoting the detonation of ammonium nitrate charges.

Munroe (82) heated 10-pound charges of ammonium nitrate over a coke fire to 375° C. in open kettles and obtained volatilization only. Kast (65) heated 600 grams of ammonium nitrate in a steel cask over a wood fire and obtained no explosion. Nuckolls (90) found that intense local heating, such as magnesium or thermit fires, did not sensitize the entire mass sufficiently to propagate an explosion.

Rapid heating, suitable confinement, and perhaps good insulation are likely to lead to explosion (33, 34, 35, 82). As pointed out in the first part of this report, of nine cases of fires in large quantities of ammonium nitrate, explosions followed in four cases. Heat and quantity alone are obviously not always sufficient to cause detonation.

When heated under confinement, the temperature at which ammonium nitrate explodes appears to be between 300° and 350° C. (40, 75). The pressure at the time of explosion has not yet been determined, due perhaps to the difficulty of making such measurements.

Elliott and associates (40) heated 38 grams of ammonium nitrate electrically in 1- by 3-inch galvanized-pipe nipples, completely confined, and obtained one rupture (at 358° C.) and one failure. The quantity here may have been too small, or the zinc in the galvanized pipe may have been a factor.

In other tests (20), 1-1/2- by 8-inch standard iron pipe was filled with ammonium nitrate fertilizer (completely confined) and thrown into a fire. The end blew off the pipe, and no explosion followed. A tightly closed, light-gage metal can containing 4 pounds of ammonium nitrate fertilizer was thrown into a fire. The cover was dislodged, and the nitrate fumed out. Ten pounds of ammonium nitrate fertilizer in a six-ply bag was placed in a fire. The bag ignited and burned, and the mixture merely fumed off.

Macy and associates (75) heated 100-pound charges of ammonium nitrate fertilizer plus paper in 1/4-inch steel boxes over a fire. The boxes ruptured. Ten pounds of ammonium nitrate fertilizer in a 5/16-inch steel container, 6 inches in diameter and 11 inches in length, was ruptured in a fire without exploding. However, when 5.7 pounds of ammonium nitrate fertilizer mixed with 0.006 pound of bag paper were placed in a bomb 2-1.2 inches by 36 inches with a wall thickness of 1/8 inch, the air removed and electric heat applied, the bomb was fragmented. These authors give the explosion temperature of pure ammonium nitrate as 325° C. (616° F.).

Five pounds of ammonium nitrate fertilizer in 1/4-inch Shelby steel tubing, 3 inches in diameter and 20 inches in length, heated electrically, detonated with fragmentation of the bomb (21).

In experimental work now being carried out by the Bureau of Mines, explosions by heat and confinement of (1) pure ammonium nitrate, (2) ammonium nitrate fertilizer of the type that exploded at Texas City and Brest, and (3) ammonium nitrate fertilizer plus 1.5 percent of paper bag container have been obtained in Shelby steel tubing, 3 inches in diameter and 20 inches in length, with and without vent openings. The charges were heated electrically. The temperatures recorded just before the explosions were 277°-334° C. for the pure ammonium nitrate, 114°-350° C. for the ammonium nitrate fertilizer, and 134°-153° C. for the fertilizer plus bag paper.

Effect of Impurities and Diluents on Explosibility

Nitric acid is said to increase the sensitivity of ammonium nitrate to explosion (34), and Munroe (82) suggested that the presence of nitric acid may have been the initiator of the Repauno and Oakdale explosions.

Organic matter, such as used in the fertilizer coatings, increases the sensitivity to explosion (7, 23, 28, 29, 33, 90).

Weduwen (113) has shown that 250 grams of a 50 : 50 mixture of ammonium nitrate and an indifferent salt can be made to explode violently by means of 50 grams of TNT.

Munroe (34, 82) found that an 80 : 20 mixture of nitrate-sulfate could be detonated with 75 grams of blasting gelatin, while a 60 : 40 mixture did not detonate with 100 grams of blasting gelatin.

When 2-kg. charges were primed with 100 grams of picric acid, no explosions or incomplete explosions were obtained in the following mixtures: 50 : 50 ammonium nitrate-ammonium carbonate; 55 : 45 ammonium nitrate-ammonium chloride; 80 : 20 ammonium nitrate-potassium chloride; 90 : 10 ammonium nitrate-potassium nitrate; 90 : 10 ammonium nitrate-calcium sulfate (33, 34, 65).

Laffitte and Parisot (71) were able to detonate ammonium nitrate with mercury fulminate in tubes 7-21 mm. in diameter when mixed with 1.5-2.0 percent of magnesium, aluminum, dinitronaphthalene, trinitronaphthalene, or TNT in quantities not exceeding 30 grams. Detonation was not complete, however, when these materials were not mixed with the nitrate.

In tests reported by Munroe (82), 10-pound charges of ammonium nitrate in solution in open kettles were evaporated to the crystallizing point, the temperature was raised to insure complete liquefaction, and detonators or blasting gelatin exploded in the mass. Although No. 8 detonators, singly and in groups of three, and 100-gram masses of explosive gelatin, primed with Cordeau, were exploded in these "hot liquors," in no instance was there detonation of the ammonium nitrate (82).

No detonations were obtained when No. 8 blasting caps were exploded in: (a) Half-pound charges of ammonium nitrate fertilizer; (b) 200 grams of ammonium nitrate mixed with 25 grams of engine oil; or (c) 100 grams ammonium nitrate mixed with 25 grams of pulverized charcoal. A half-pound charge of ammonium nitrate fertilizer placed in a 2-inch pipe open at the top was not completely detonated when 20 grams of 60-percent dyanmite were used as a booster (20).

Inert material decreases the explosibility of ammonium nitrate (34, 35). Ammonium sulfate or powdered limestone is said to have this effect (89). Kast (65) states that ammonium nitrate-ammonium sulfate mixtures decompose exothermically down to about 40 percent nitrate. He gives -150,200 calories for the reaction

$$4\ NH_4NO_3 + 2(NH_4)_2SO_4 = 16\ H_2O + 2\ SO_2 + 6\ N_2.$$

Bassett and Durrant (8) found that ammonium nitrate, when reacting with copper, formed $Cu(NH_3)_4(NO_3)_2 + Cu(NC_3)_2\ 3\ Cu(OH)_2$, and small amounts of nitrite, both of which increased the sensitivity of ammonium nitrate to detonation.

Davis (33) quoted tests performed by the Consolidated Mining & Smelting Corp. and reported by the Allied War Supplies Corporation, in which 20 grams of ammonium nitrate were dropped on a thin steel plate floated on molten lead or tin. When the tin bath was used, the point at which the ammonium nitrate ignited without explosion was 464°-478° C. With the lead bath, it was 510°-580° C. They also found no appreciable difference between pure ammonium nitrate and coated ammonium nitrate.

Nuckolls (90) found that pure ammonium nitrate could be decomposed with flame at a temperature of 395°-396° C. For a "petrolated" product, the temperature was 380° C.

When mixed with 5-10 percent of nitrostarch, explosions occur at 150° C. without warning (92).

SUMMARY

The following summary is based upon the foregoing experimental observations by different investigators and upon their conclusions.

1. Chemically pure ammonium nitrate does not decompose spontaneously at ordinary temperatures.

2. It is an oxidizing agent and, as such, may react with reducing materials, such as carbonaceous matter, certain metals, phosphorus, sulfur, etc. Such mixtures may lead to spontaneous heating and the temperature at which this may take place is governed by the specific materials concerned and their environment. With certain mixtures and the proper environment, spontaneous heating can occur at ordinary temperatures.

3. The quantity of ammonium nitrate that can be detonated by initiation depends upon the geometry, confinement, temperature, packing density, nature and quantities of any impurities present, and strength of the booster charge.

4. It is considered very difficult to detonate by ordinary impact or friction, although some experimental results appear to be at variance with others.

5. When heated unconfined, it merely effervesces and leaves little, if any, residue.

6. When heated under confinement, or partial confinement, it may explode. The temperature at which explosion occurs is affected by a number of factors, such as the container, heating rate, and impurities present. For pure ammonium nitrate, temperatures from 300° to 350° C. have been variously reported. The temperature is lowered by the presence of certain impurities. Pressures necessary for explosion have not been determined.

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